An attempt to synthesize Ga$_{1-x}$Mn$_x$As by low temperature liquid phase epitaxy

S. S. Chandvankar[a†], A. M. Narsale[b], A. P. Shah[a], Bhavtosh Bansal[a] and B. M. Arora[a]
[a]Department of Condensed Matter Physics & Materials Science,
Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai- 400 005, India.
[b]Department of Physics, University of Mumbai, Vidyanagari, Mumbai - 400 098, India.
E-mail: sschand@tifr.res.in

ABSTRACT

Single layers of Ga(Mn)As have been grown on GaAs substrates at low temperature (~650^{0}C) by liquid phase epitaxy using two types of gallium rich solutions viz. (1) solutions saturated with weighed GaAs pieces and (2) solutions saturated using a separate saturating GaAs substrate. Mn metal (upto 6% by weight) is added to solutions. In both cases, with about 2% Mn in the solution, layers are n-type, whereas beyond this value, the grown layers are p-type. The hole concentration tends to saturate at ~10^{18}cm^{-3} with about 6% Mn in the solution. Electro-chemical voltage (ECV) etch profiles indicate diffusion of Mn well beyond the thickness of the grown layers. However, x-ray and photoluminescence measurements do not indicate significant incorporation of Mn in the GaAs layer.

Key words: Liquid phase epitaxy, Mn doping, Ga(Mn)As.

1. INTRODUCTION

Dilute magnetic semiconductors (DMS) are potential candidates for technological applications in semiconductor 'spintronics' [1] that utilizes both charge and spin properties of electrons (holes). Hole doped Ga(Mn)As is one interesting material system for such applications. Most of the reports investigating thin layers of this material system are based on synthesis using molecular beam epitaxy (MBE) [2]. Various reports suggest that incorporation of about 2% Mn in GaAs is necessary to observe appreciable magnetic moment [3]. Recently, GaMnAs thin films with significant Mn incorporation have been grown at ~850^{0}C using liquid phase epitaxy [4]. Mn impurity has large diffusion coefficient in GaAs ~5x10^{-12}cm^{2}sec^{-1} [5]. Therefore it is desirable to lower the growth temperature. However, there is no report of growth of Ga(Mn)As by LPE at low temperatures. In this paper, we report our trials for the growth of Ga(Mn)As single layers at 650^{0}C.

2. EXPERIMENTAL

All the growth experiments are done using piston graphite boat [6] shown in Fig.1. As seen, the boat contains four parts: a substrate holder, a disposal bin for the used solutions, housing for piston and a tray to carry solutions. The movements of the piston, solutions and the substrate holder are carried out externally by using 2mm diameter molybdenum rods fitted with the end cap. This boat can be used to grow structures containing ten layers. In this boat design, the growth solution is squeezed through the channel when pushed by the piston. The growth experiments are carried out in a resistively heated gold-coated semi-transparent furnace in high purity hydrogen gas ambient. In a typical growth experiment, a chemically

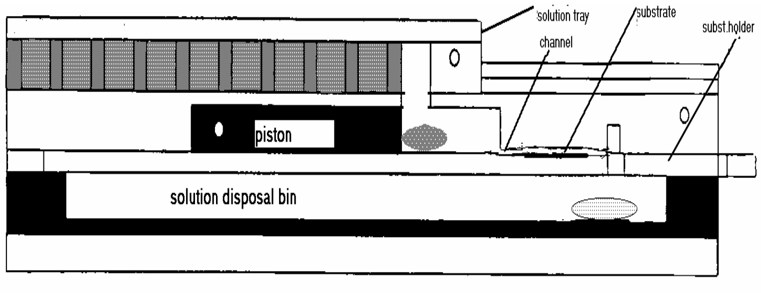

Fig.1 Schematic of the piston graphite boat

etched semi-insulating GaAs substrate is placed in the recess in the slider. The slider is held between the upper graphite housing carrying the piston and the lower housing containing the disposal bin for collecting the used solutions. There is a gap of about 0.5 mm above the substrate where the growth solution resides during its usage for the epi-layer growth. A solution of desired composition is placed in the oval shaped slot in the solution carrier. It consists of 2.5g gallium of 6N purity and required amount of arsenic for saturating the solution at 660^0C. Piston has another recess on top surface in which substrate for solution saturation can be placed. After loading the substrate and the solution, the furnace is purged with pure hydrogen for several hours. During the growth, the furnace is heated to about 680^oC and held for one hour to ensure homogenization of the solution. The furnace is then slowly cooled, typically at a rate of ~1.5^oC/min. At about 650^0C, the solution is brought in contact with the substrate as explained above. After 35 minutes, the grown wafer is pulled out using a molybdenum rod attached to the substrate carrier.

We have done two sets of experiments. In the first set, solutions saturated with weighed GaAs pieces are used. At 660^0C, amount of GaAs required to saturate 1gm gallium is 7.3mg. Such a solution contains 99.6% gallium and 0.4% arsenic. Using this information, a solution is prepared and used to grow a single undoped GaAs layer using the procedure outlined above. Several solutions with same arsenic amount but increasing amount of Mn are prepared for subsequent growth experiments. A single Ga(Mn)As layer is grown from each solution following the same growth schedule. In the second set of experiments, solutions saturated using a separate saturating GaAs substrate are used. GaAs substrate is placed in the recess made at the top of the piston. An accurately weighed portion of gallium is placed in contact with this substrate at 660^0C, for one hour. This exactly saturated solution is used to grow a GaAs layer. Weight loss of the saturating substrate is used to estimate the amount of GaAs dissolved in the solution. Subsequently, several solutions containing gallium and increasing amount of Mn are prepared and saturated using a saturating GaAs substrate. Each of these solutions is then used to grow a single Ga(Mn)As layer. In both sets of experiments, Mn upto 6 weight % is used in the solutions.

Thickness of the grown layer is observed using optical microscope with cleaved and stained cross-section of each sample. Bio-Rad ECV profiler is used to record the doping density of the layer as a function of depth. This measurement also gives carrier (n/p) type. Hall measurements are used for measuring doping density and mobility of the layers. X-ray diffraction measurements are done to check presence of any Ga(Mn)As with lattice parameter significantly different from that of GaAs. Photoluminescence measurements are used to check optical quality and Mn incorporation in the layer.

3. RESULTS AND DISCUSSION

All the layers grown by the LPE process described above have mirror smooth surfaces. The results of growth experiments establish that the amount of arsenic required to saturate Ga solvent increases with Mn added in the solution. This is shown in Fig. 2 where we have plotted the amount of GaAs etched from the saturated substrate during saturation at 660^0C with varying amount of Mn in the Ga solvent. This leads us to conclude that in the method of preparing the solution with fixed amount of GaAs added to the Ga solvent (as needed for preparing a saturated solution with no Mn) the solution will be undersaturated. Contact of such solution with the growth substrate would most likely etch the substrate initially before the growth commences as cooling is continued. Measurements of the thickness of the grown epi-layers obtained by cleaving and staining technique were unusual. The epi-layers grown from exactly saturated solutions were found to be thinner than those grown from the solutions prepared by adding fixed amount of GaAs as shown in Fig. 3. An understanding of this unusual behavior has been

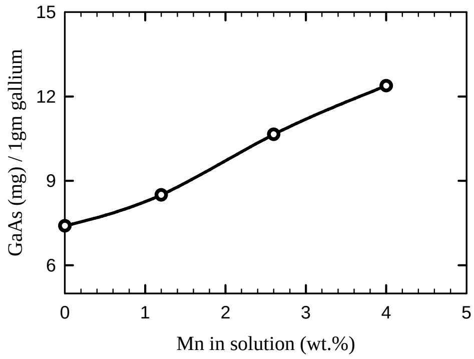

Fig.2 GaAs (mg)/gm gallium for increasing Mn in solution.

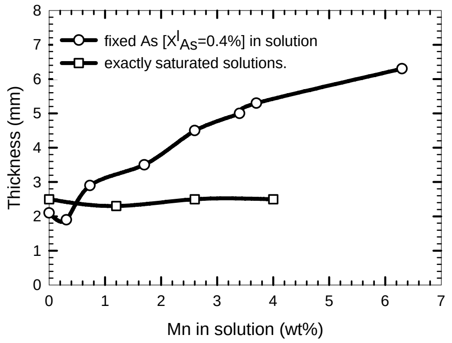

Fig.3 Thickness of epi layers

sought in terms of anomalous diffusion of Mn into GaAs when Ga+Mn solvent or undersaturated Ga+Mn+GaAs solution contacts the GaAs substrate. Figure 4 shows the electrochemical etch profile of three samples grown from exactly saturated solutions, 04hs22 with no Mn in solution, 04hs19 with 1.2%Mn and 04hs21 with 4%Mn in solution. As seen, although measured thickness in all three samples is ~2.5μm, etch profile extends beyond 4μm in case of Mn doped samples, as against undoped sample 04hs22. This anomalous behavior is seen in ECV etch profiles of samples grown with Ga+Mn+fixed amount of GaAs in the solution. Etch profile of the GaAs substrate used for solution saturation also shows this behavior. Thus, because of Mn diffusion into the epi-layer as well as GaAs substrate, estimation of grown epi-layer thickness by cleave-stain procedure is unreliable. Depending on the profile of Mn or discontinuity in the concentration, measured thickness may be larger than the actual epi-layer growth. A more detailed analysis of this behavior is required for better understanding.

Another unexpected result of these experiments is the nature of the doping type resulting from the incorporation of Mn into GaAs. Mn substituting for Ga is supposed to produce p-type doping. Our undoped GaAs layers are n type (~10^{17}cm^{-3}) with perhaps Si as the background dopant. Layers grown with less than 2% Mn in Ga solvent, turned out to have enhanced n type conduction. This is seen in both ECV profiling (Fig. 4) as well as in the Hall measurements presented in Tables 1 and 2. Layers from Ga solvents having more than 2% Mn turned out to be p type. However in all the samples grown by us, the p-type doping level remained below 10^{18}/cm^3. The concentration level obtained from Hall measurements is an average number as seen from concentration profile obtained from ECV measurements. It is possible that there is a strong tendency for Mn to enter into the GaAs sublattice into interstitial position which has been speculated to produce n type doping.

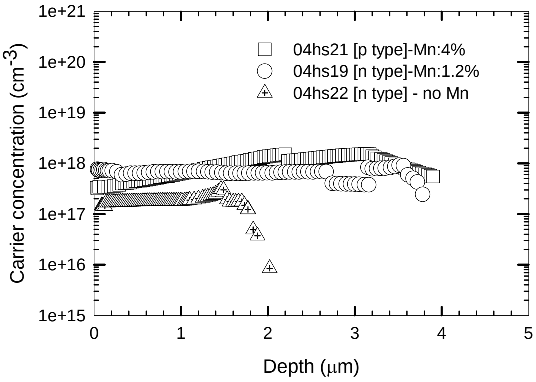

Fig.4 ECV profiles of epi-layers with and without Mn in solution

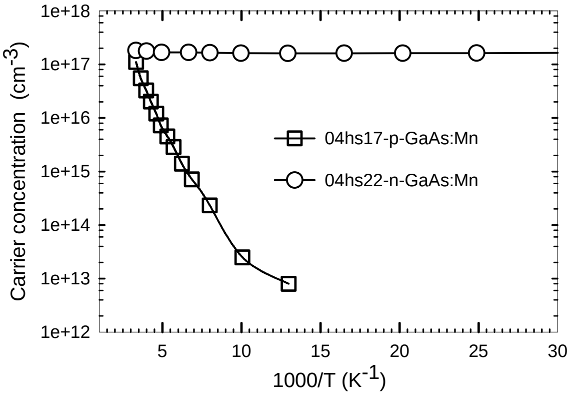

Fig.5 Plots of temperature dependent carrier concentrations in Mn doped samples.

Table 1. Mobility and carrier concentration of layers grown with fixed amount of As in the solution.

Sample no.	Mn wt %	Carrier mobility cm^2/v-s	Carrier type concn.(cm^{-3})
04hs16	-	3120	(n) 5.7x10^{17}
04hs14	0.31	2063	(n) 1.8x10^{18}
04hs07	0.73	1877	(n) 1.1x10^{18}
04hs13	1.70	1311	(n) 2.5x10^{17}
04hs15	2.60	184	(p) 3.8x10^{16}
04hs17	3.40	171	(p) 1.8x10^{17}
04hs09	3.90	156	(p) 1.6x10^{17}
04hs11	6.30	185	(p) 2.1x10^{17}

Table 2. Mobility and carrier concentration of layers grown using a separate saturating GaAs substrate for saturation.

Sample no.	Mn wt %	Carrier mobility cm^2/V-s	Carrier type concn.(cm^{-3})
04hs22	-	3892	(n) 1.8x10^{17}
04hs20	-	2977	(n) 6.8x10^{17}
04hs19	1.20	1595	(n) 7.4x10^{17}
04hs18	2.60	156	(p) 5.5x10^{16}
04hs21	4.00	158	(p) 2.3x10^{17}

As such, both types of incorporations (Mn on Ga site and interstitial Mn) coexist and the material is heavily compensated. The net doping type would depend on relative predominance of Mn_{Ga} and Mn_i concentration, which seems to change with the amount of Mn in the growth solution. Fig. 5 shows plots of temperature dependant Hall measurements of Mn doped n-type layer (04hs22) and a p-type layer (04hs17). As seen, carrier density does not vary with temperature for n-layer, whereas for p-layer, this measurement confirms the presence of an acceptor level with activation energy (E_A) for acceptors, estimated to be ~110meV. Hall measurements also indicate that both the electron and hole concentrations tend to saturate at about

10^{18}cm^{-3} with 0-6% Mn in the solution. This is considerably less than the hole concentration level achieved (~10^{21}/cm^3) in MBE grown Ga(Mn)As [7]. Fig. 6 shows low temperature photoluminescence spectra of undoped and Mn doped layers. It is seen that Mn incorporation into the grown layer quenches the band to band emission and a broad band characteristic of Mn in GaAs appears. There is not much difference in the PL spectra of samples that are n type or p type. This behavior may be expected as both types of samples are compensated and emission may involve both donors and acceptors. We tried to find out if there was a Ga(Mn)As phase by carrying out x-ray diffraction measurements in these samples. We saw predominantly the same signatures as observed on samples with no Mn. These measurements indicate that the total amount of Mn incorporated is insufficient to produce a Ga(Mn)As layer with significantly large amount of Mn.

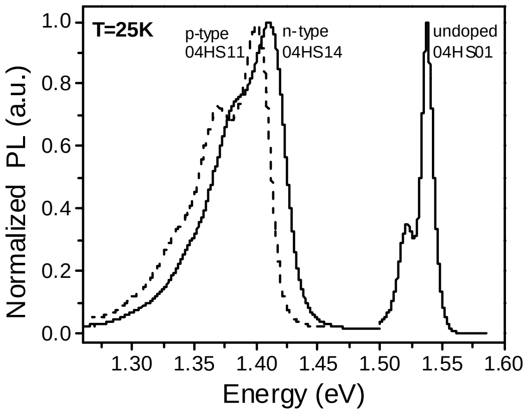

Fig.6 Photoluminescence spectra of Mn doped GaAs.

4. CONCLUSIONS

We have attempted to synthesize (GaMnAs) using low temperature liquid phase epitaxy. Two sets of experiments have been done using different solution saturation schemes. Electrical measurements show that with about 2% Mn in the solution, Mn seems to enhance the n-type carrier density (~10^{18} cm^{-3}) in the epi-layer. This suggests a significant incorporation of Mn as a donor presumably as an interstitial. However, beyond 2% Mn in the solution, the layer turns out to be p-type indicating Mn predominantly substituting for gallium at higher concentration of Mn in the solution. Electro-chemical voltage (ECV) etch profiles indicate diffusion of Mn well beyond the thickness of the grown layers. Temperature dependant Hall measurements of p-type layer confirms the presence of an acceptor level with E_A~110meV. The hole concentration tends to saturate at ~10^{18}cm^{-3} with about 6% Mn in the solution. PL measurements show a broad band centered at 885-900 nm characteristic of Mn doped GaAs. Thus, growth at 650^{0}C by LPE does not seem to incorporate sufficient Mn in the layer suitable for significant magnetic moment.

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